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AC AND DC ELECTRICAL PROPERTIES OF TETRAPYRAZINO-PORPHYRAZINE VANADYL (IV)

NAZAR A. HUSSIEN

Department of Chemistry, College of Education for Pure Sciences, University, Basra, Iraq

ABSTRACT

Ac and dc conductivities of thin film of Vanadyl complex of tetrapyrazino porphrazine were carried out at different temperatures and different frequencies. The study shows a semiconducting properties and frequency dependence conductivity. It shows that the ac conductivity of the complex is higher than it's dc conductivity due to the sum of the temperature and frequency dependence for the ac conductivity. The density of states around Fermi level[$N_{(EF)}$)], between which the electrons hope, were estimated using Mott and Davis relation and it has a value of about 1.1×1029 ev-1cm-3.

KEYWORDS: Tetrapyrazinoporphrazine Vanadyl Complex. Ac and Dc Conductivity

INTRODUCTION

Studies on the temperature dependence of the electrical conductivity have revealed departure from simple Arrhenius behavior which have been interpreted as a result of the existence of states in the band gap(around Fermi level)[(1)].

Ac conductivity measurements have been widely assumed the existence of localized sites between which electrons can hop in response to alternating field [(2)]. The band conduction is either frequency independent(dc, dark conductivity, σ_{dc}) or frequency dependent, σ_{ac}, as in the relation:

$\boldsymbol{\sigma_{ac}\ \alpha\ \omega^{n}}$, where n is constant and ω is the angular frequency[(3)].

The ac conductivity (σ_{ac}) tends to dominate at high temperatures and high frequencies. The measured ac conductivity is a sum of ac and dc conductivities (σ_T)[(2)],

$\sigma_T = \sigma_{dc} + \sigma_{ac}$

σ_{dc} can be expressed by the Arrhenius like equation[(4,5)],

$\boldsymbol{\sigma_{dc} = \sigma_0\ e^{\frac{\Delta E}{kT}}}$ where ΔE is the activation energy between valance and conduction bands, k is Boltzmann constant, T is the temperature is Kevin and σ_0 is pre-exponential factor.

Studying of ac and dc electrical conductivity were carried out by many workers [(1, 2, 6, 7)].

In this work the ac and dc conductivities were carried out for Tetrapyrazino porphrazine complex with Vanadyl(ɪv).

Experimental

The chemicals were used as it was supplied except pyridine and Quinoline were distilled twice for each.

- **Synthesis of 2,3-dicyano pyrazine[8] DCP)**

1 ml of glyoxal was dissolved in a mixture of 25 ml of ethanol and 25 ml of acetic acid and added to a conical flask fitted with condenser and containing 2.36g (0.0218mol) diaminomalonitrile(DAMN) dissolved in 25 ml ethanol. The mixture then refluxed for 4 hours and left for two day to settle down. The precipitate then filtered and re-crystallized from mixture of hexane and acetone (1:1) ratio. The yield is 2, 3-dicyanopyrazino, 0.73g (35%) as dark brown powder. The synthesis is shown in figure 1.

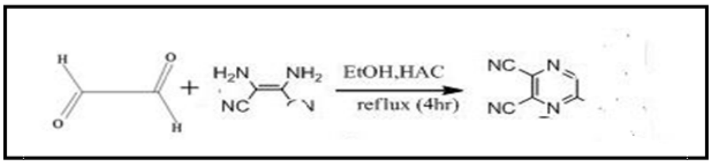

Figure 1: Synthesis of DCP

Synthesis of Tetrapyrazinoporphyrazine Vanadium Oxide Complex (Pzvo)

A mixture of anhydrous Vanadyl sulfate pentahydrate(1.33g , 5.1 x10^{-4} Mol) , 2,3-dicyanopyrazine (0.265g , 2.04x10^{-3}mol), Urea (0.22g, 2.04 x10^{-3}mol) and 8 ml of quinoline was refluxed for 4 hours[9,10]. The reaction mixture was cooled and the crude reaction product was purified by dissolving it in a least amount of chloroform (nearly 2 ml) and re-precipitated by adding it drop wise with stirring to a beaker containing 100 ml ethanol. The yield is 0.82 gm (68.5%), bluish powder. CHN ($C_{24}H_8N_{16}VO$): calcd; C: 49.07, H: 2.73, N: 38.16; Found; C: 48.70, H: 2.62, N: 38.02. The synthesis is shown in figure 2.

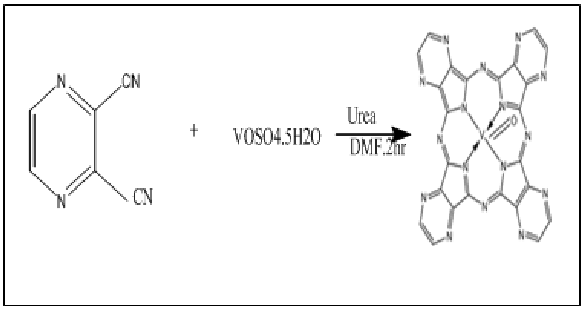

Figure 2: Synthesis of PzVo

RESULTS AND DISCUSSIONS

Figures 3 and 4 show the IR spectra of both DCP and the complex PzVO respectively The –CN stretching at 2250 cm^{-1} in the DCP spectrum disappeared in figure 4 as a result to the formation of the complex PzVO[11].

Figure 5 shows the Uv-Visible spectra, it shows the characteristic Soret band at 440 nm and the Q band at 640 nm. Which are attributed to the (π- π*) of the delocalized electrons in the ring and (n-π*) transition which belongs to the hetro-aromatic system of the tetraparazino porphyrazine ring [5].

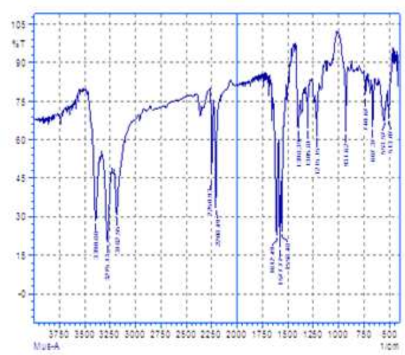

Figure 3: IR Spectrum for DCP (KBr Disc)

Figure 4: IR Spectrum for PzCo

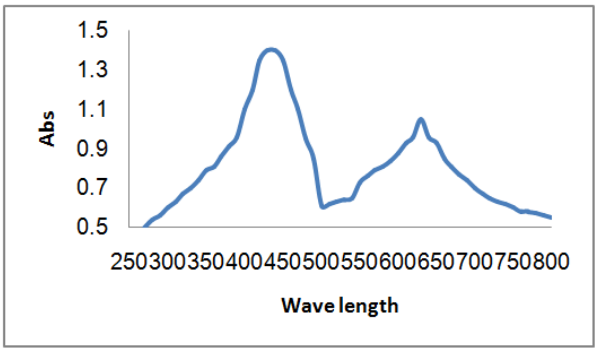

Figure 5: The UV-Visible Spectrum of PzVo in Dmf

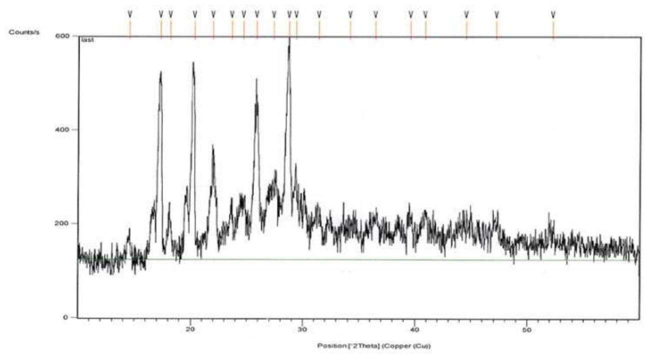

Figure 6: X-Ray Diffraction of PzVO

Electrical Conductivity

The dc electrical conductivity measurements were carried out using surface cell and using a system consists of cryostat connected to voltmeter and ammeter to measure the voltage and current respectively with power supply to for heating. The ac conductivity measurements were carried out using 4800A vector impedance system and same cryostat used for the dc conductivity at different temperatures (303-403 K) and at different frequencies (5000-50000) Hz.

Figure 1 shows the variation of current with voltage for the complex at different temperatures.

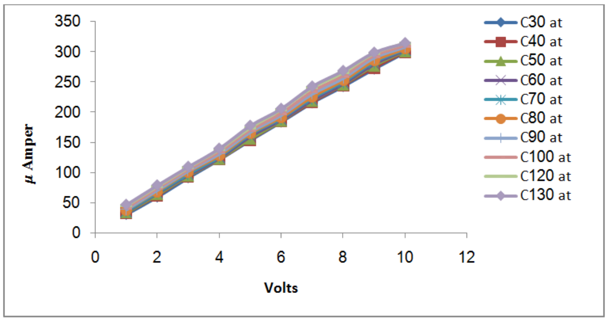

Figure 7: Variation of the Current with Voltage at Different Temperature for the Complex

It shows the linear (ohmic) relation for the used voltages at the different temperatures. For the electrical measurements, the average voltage of 7 volts was used as constant voltage.

Figure 2 shows the $-\ln ln\sigma$ ($where\ \sigma\ is\ the\ specific\ conductivity$, $ohm^{-1}.cm^{-1}$) at different temperatures, it gives a linear relation with slope of 0.1449(activation energy of 0.56 eV at 296 K)

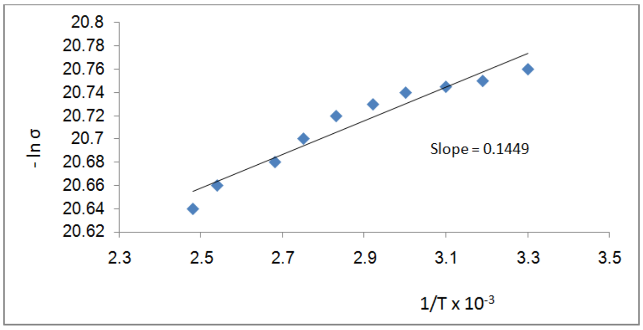

Figure 8: The Variation Od Dc Electrical Conductivity($ln\sigma$) With Temperature for the Vanadyl Complex at Different Temperatures

Figure 3 shows the ac electrical conductivity of the Vanadyl complex at different frequencies and different temperatures**.** It shows that the conductivity increases slightly at low frequencies at the different temperatures but it highly increases at high frequencies and temperatures. This is due to the higher rate of hopping between states around Fermi level in between the valance and conduction bands [1, 2, and 12].

The relation between ac conductivity and frequency is explained by the relation [3]:

$\boldsymbol{\sigma ac = \omega^{n}}$ where n is constant.

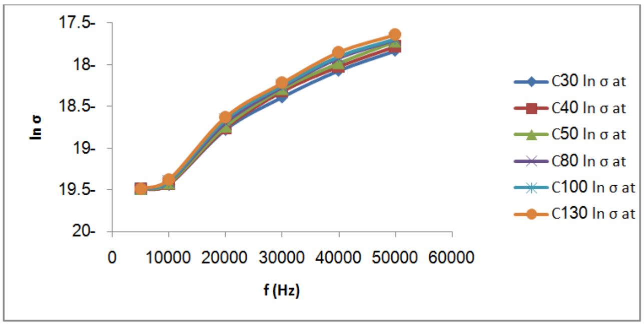

Figure 9: The Variation of Ac Conductivity ($ln\sigma$) with Linear Frequency (in Hz) at Different Temperatures

Figure (4) shows the variation of ac conductivity with angular frequency at different temperatures ($\boldsymbol{ln\omega}$) ($\boldsymbol{\omega = 2\pi f}$). It shows the same relation behavior as in the figure (3) there is no variable difference between angular frequency and linear frequency.

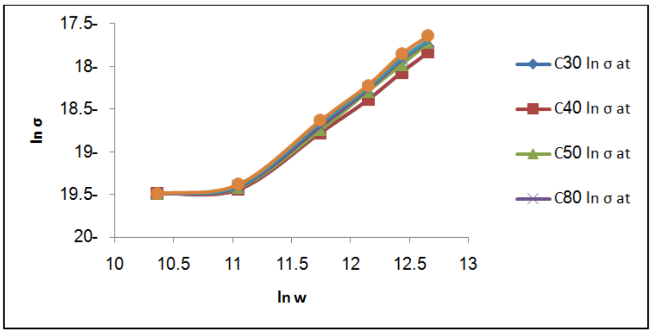

Figure 10: Variation of Ac Conductivity with Angular Frequency at Different Temperatures

Figure 5 shows the variation of dc and ac conductivities with temperature and at different frequencies (for ac conductivity). It shows that the ac conductivities are higher than the dc conductivity which is because that the measured ac conductivity is in fact a sum of dc and ac conductivities, i.e, the ac conductivity is explained by two mechanisms ac and dc[2].

$$\boldsymbol{\sigma ac(T) = \sigma ac + \sigma dc}$$

Ac due to hopping of carrier charges(electrons) between the states around Fermi level, while the dc conductivity is due to charge carried transfer from lower state to higher state, the law activation energy calculated from the slope of the dc conductivity refers that the dc conductivity is either **n** or **p**- types.

The n-type which from Donor level to the conduction band or p-type which is from valance band to the Acceptor level [5]

The states around Fermi level can be calculated from Mott and Davis

Relation [2, 13]

$$\boldsymbol{\sigma ac = \frac{4\pi}{3}(ln2)e^2 kT[N_{EF}]^2\alpha^{-5}\left[\ln\frac{\vartheta ph}{\omega}\right]^4\omega}$$

Where N_{EF} are the number of states around Fermi level, α is the reciprocal-spacing (calculated from the x-ray

diffraction, figure 6, where the position of the highest peak is 25.78($^{0}2\theta$) which is estimated to be 3.4$\AA$.

$\mathbf{N_{EF}=1.1\times10^{28}\ eV^{-1}\ .cm^{-3}}$.

ϑ_{ph} Is the phonon frequency (1×10^{12} Hz)[(2)]. σac Is the pure ac conductivity after subtraction of dc conductivity?

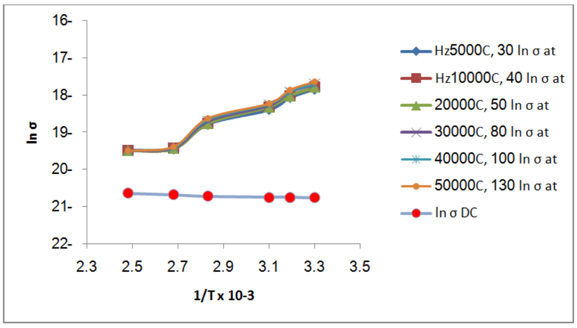

Figure 5: The Variation of Dc and Ac Conductivity with Temperatures and at Different Frequencies for Ac Conductivity

CONCLUSIONS

The ac and dc electrical conductivities shows that Tetrapyrazino porphrazine Vanadyl(Iv) complex has semiconducting properties. It's ac conductivity is higher than It's dc conductivity and the estimated number of statutes around Fermi level is about $\mathbf{1.1\times10^{28}\ eV^{-1}\ .cm^{-3}}$.

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